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## FTIR SPECTROSCOPIC STUDY OF S-METOLACHLOR SORPTION ON INORGANIC AND ORGANICALLY MODIFIED MONTMORILLONITE FROM BOGOVINA

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### Abstract

Environmental problems related to the application of herbicides are causing a concern due to their increasing presence in soil, groundwater and surface water. Numerous methods have been developed in order to reduce herbicide mobility and protect natural water resources. The results presented in this paper show the interaction of herbicide S-metolachlor with inorganic and organically modified montmorillonite from Bogovina (Boljevac municipality, Serbia). Clay sample from Bogovina represents Ca-Na montmorillonite with a small amount of quartz, cristobalite and carbonate minerals. Organic montmorillonites were obtained after modification with different concentrations of organic complex (HDTMA and PTMA), whereas inorganic modification was performed with 1M NaCl solution. The interaction between minerals and herbicide was monitored using infrared spectroscopy. IR bands observed in the inorganic modified montmorillonite (Na-montmorillonite) are typical for smectites with a high Al content in the octahedron position.

The intercalation of HDTMA<sup>+</sup> cations into the interlayer space produces redshift of the IR bands that originate from the vibrations of the adsorbed water, as a consequence of the hydrogen bond strength reduction in HDTMA-montmorillonite. Also, the intensity of these bands decreases significantly with the increasing concentration of HDTMA<sup>+</sup> cation. All these changes are related to the decreasing of the water content in the interlayer space by increasing the content of HDTMA. The occurrence of the stretching CH<sub>2</sub> vibrations is generally the main difference in the spectrum of HDTMA modified montmorillonite in comparison with the spectrum of inorganically modified montmorillonite. The wavenumber, intensity and width of these bands are sensitive to conformation in hydrocarbon chains. After the organic modification of the montmorillonite with the PTMA complex, stretching vibrations of the phenyl ring occurred.

Analysis of FTIR spectroscopy data showed that the hydrogen bond is one of the most important mechanisms that occur between Na-montmorillonite and S-metolachlor. Comparing the FTIR spectra of herbicides before and after the sorption, it can be concluded that the carbonyl group participate in the binding process. Sorption of S-metolachlor on HDTMA-montmorillonites causes the redshift of the C=O absorption band. Shifting to lower wavenumbers and joining with the deformation vibration band of water indicates that the C=O group participated in the formation of a bond with the montmorillonite. Sorption of S-metolachlor molecules on PTMA-montmorillonite takes place through the interaction between the aromatic benzene ring of S-metolachlor and the aromatic benzene ring of the organic complex ( $\pi$ - $\pi$  bonds). Also, the formation of a hydrogen bond occurs between the molecules of S-metolachlor and the molecules of water



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that are in the interlayer space and/or oxygen on the surface of the tetrahedral sheet of the montmorillonite.

Keywords: adsorption, S-metolachlor, HDTMA, PTMA, infrared spectroscopy

## INTRODUCTION

The high solubility of some herbicides negatively affects their efficiency and therefore causes serious environmental problems due to the migration into groundwater (Cohen et al., 1986). The reduced inhibitory activity requires repetition of treatment, which leads to increased costs and a negative impact on the environment.

Therefore, attempts were made to create a formulation that would lead to an improvement in the inhibitory activity of herbicides, which will also reduce their migration to groundwater. Certain experiments involved creating a stronger interaction between the mineral surface and the herbicide by making organo-mineral complexes. Montmorillonites previously modified with aromatic or aliphatic organic cations showed better sorption of certain nonionic herbicides than those without any modifications (El-Nahhal et al., 1999). S-metolachlor, herbicide belongs to the chloroacetanilide group, and is often used to control annual grass and broadleaf weeds in crops of corn, soybeans, sugar beets, sunflowers, etc. The groundwater concentrations vary from 0.08 to 680  $\mu\text{g/mL}$  (Chesters et al., 1989). Neutral degradation products of S-metolachlor may possess a certain dose of toxicity similar to parent herbicides (Hladik et al., 2006).

Montmorillonite is a clay mineral widely used in various industries due to its specific physical and chemical properties, such as cation exchange capacity (CEC), large surface area, high pore volume, high swelling ability, etc. Intercalation of organic complexes into montmorillonite layers changes surface properties from hydrophilic to hydrophobic.

The results presented in this paper show that FTIR spectroscopy can be a valuable technique to examine the organic modification of montmorillonite as well as the interaction of herbicide S-metolachlor with inorganic and organically modified montmorillonite from Bogovina (Boljevac municipality, Serbia).

## MATERIALS AND METHODS

### Materials

HDTMA-bromide was obtained from Alfa-Aesar Chemical Company (Karlsruhe, Germany), with a purity of 98%. Phenyltrimethylammonium chloride (PTMA) was supplied by the Tokyo Chemical Industry Company (Toshima, Kita-Ku, Tokyo, Japan), with a purity of 98%.

A raw natural sample of bentonite was collected from the Bogovina locality (Serbia). Clay fraction, with montmorillonite as the dominant mineral, was separated using the decantation method. Clay fraction (< 2 mm) was then treated with 30% hydrogen peroxide in order to remove organic matter from the sample.



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After air drying, montmorillonite was saturated with 1 M NaCl, and left on a mechanical shaker for 24 h, centrifuged and rinsed with distilled water until the negative reaction on Cl<sup>-</sup>. The sample was then air-dried and named Na-montmorillonite (NaM). The cation exchange capacity (CEC) of Na-montmorillonite was 69 mmol/100g, determined using Cu-trien (triethylenetetramine) complex (Meier and Kahr, 1999), which was recommended by the Clay Mineral Society.

Na-montmorillonite was then organically modified using two organic complexes: hexadecyltrimethylammonium bromide and phenyltrimethylammonium chloride. The organoclay complexes were prepared by dropwise addition of 100 mL of HDTMA or PTMA aqueous solution, with appropriate concentration of organic complex, into the aqueous suspension of the NaM clay. Four different concentrations of organic cations were selected for the monitoring of the herbicide adsorption: 17.25 mmol/100 g of Na-montmorillonite (25% of CEC), 34.5 mmol/100 g of Na-montmorillonite (50% of CEC), 51.75 mmol/100 g of Na-montmorillonite (75% of CEC), and 69 mmol/100 g of Na-montmorillonite (100% of CEC). The reaction mixture was continuously stirred on the magnetic stirrer, at the temperature of 50°C. After the modification, the suspension was further agitated for 24 h and centrifuged at 7,000 rpm. All the samples were rinsed five times with distilled water and accordingly labelled as 1H- 0.25 CEC saturated with HDTMA complex, 2H- 0.5 CEC saturated with HDTMA complex, 3H- 0.75 CEC saturated with HDTMA complex, 4H- 1 CEC saturated with HDTMA complex, 1P- 0.25 CEC saturated with PTMA complex, 2P- 0.5 CEC saturated with PTMA complex, 3P- 0.75 CEC saturated with PTMA complex, and 4P- 1 CEC saturated with PTMA complex. All samples are then treated with 1000 mg/L working solution of S-metolachlor and marked as NaM-SM, 1H-SM, 2H-SM, 3H-SM, 4H-SM, 1P-SM, 2P-SM, 3P-SM, and 4P-SM.

### FTIR spectroscopy

All samples were investigated using FTIR method (Fourier-transform infrared spectroscopy). All results were obtained in Laboratory for infrared spectroscopy at the Faculty of Science, University of Kragujevac on a infrared spectrometer (Equinox 55, Bruker Optics) equipped with a single reflection diamond ATR accessory (Dura Sample IR II, SensIR). The samples were prepared in a form of KBr disk, and the spectra (averaged on 32 scans) were collected in the range of 4000-450 cm<sup>-1</sup>, at a resolution of 4 cm<sup>-1</sup> with corrections for the effect of the radiation wavelength on the penetration depth. For a better interpretation of the absorption bands, second derivatives were obtained for all samples.

## RESULTS AND DISCUSSION

### FTIR spectroscopy of samples without S-metolachlor

Detailed information on the interactions between S-metolachlor and the inorganic and organic montmorillonite was obtained by using infrared spectroscopy. In the spectrum of NaM (Fig. 1a), the absorption band at 3626 cm<sup>-1</sup> was assigned to stretching vibrations of structural OH groups, while the absorption bands at 3447 cm<sup>-1</sup> and 1643 cm<sup>-1</sup> were assigned to stretching and bending vibrations of water molecules in interlayer space



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(Tomić et al., 2015). The most intensive band in the spectrum at  $1034\text{ cm}^{-1}$  was assigned to stretching Si-O vibrations of the tetrahedral sheet. Absorption bands, which originate from Al-Al-OH and Al-Fe-OH bending vibrations, are located around  $916$  and  $871\text{ cm}^{-1}$ , and they are typical for mineral montmorillonite (Madejova, 2003; Tomić et al, 2012).

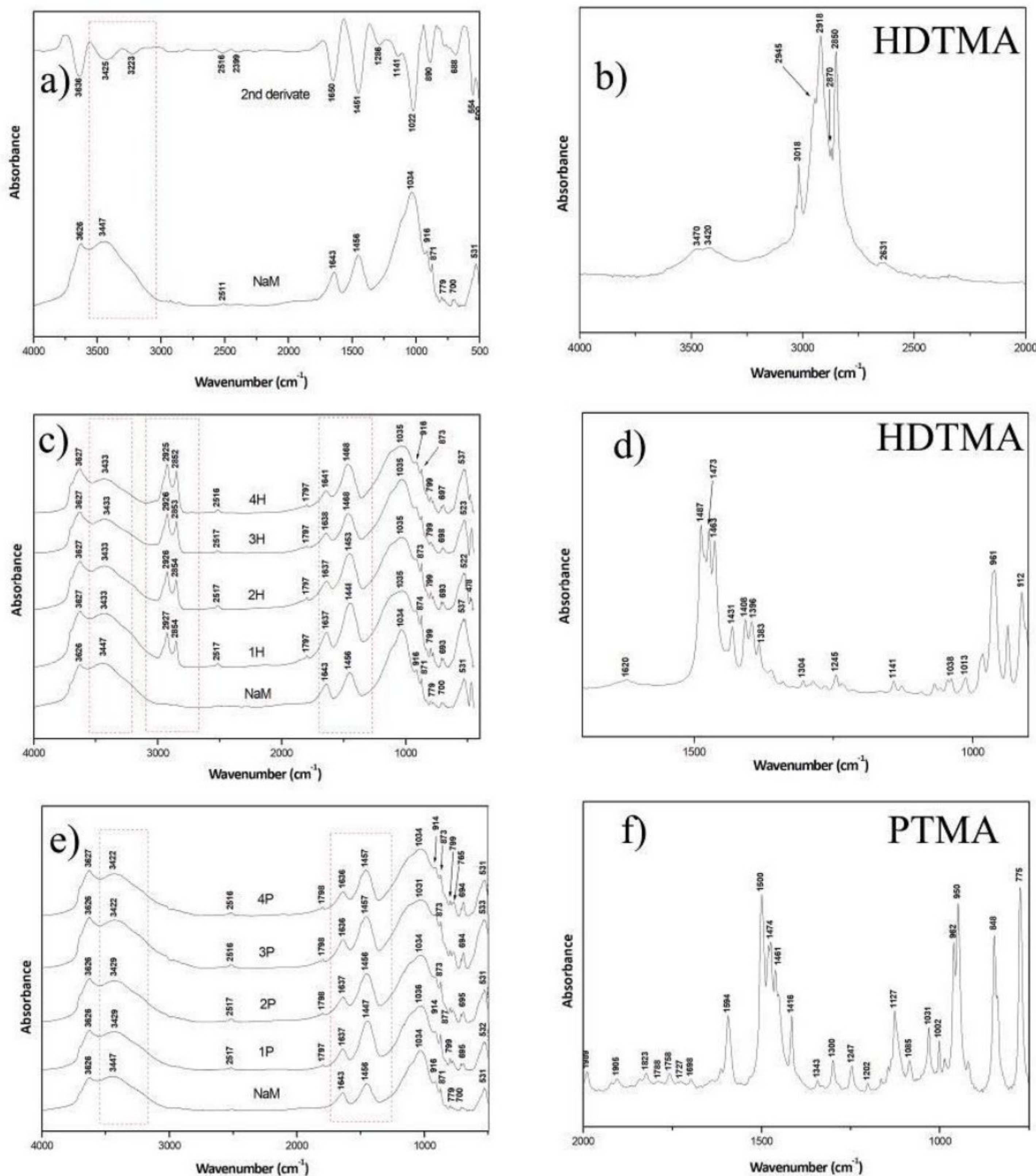


Figure 1. FTIR spectra of a) Na -montmorillonite; b) and d) HDTMA bromide; c) montmorillonites modified with different concentrations of HDTMA cation; e) montmorillonites modified with different concentrations of PTMA cation; f) PTMA chloride.

Absorption bands at  $799$  and  $779\text{ cm}^{-1}$  indicate the presence of cristobalite (Madejova and Komadel, 2001).

The band at  $1456\text{ cm}^{-1}$  indicates presence of carbonate minerals in the sample (Jović-Jovičić et al., 2008). Much better band position accuracy, as well as a sharper spectrum image can be obtained in the ATR 2nd derivative spectrum. A broad band at  $3447\text{ cm}^{-1}$  in the spectrum of the Na-montmorillonite obtained using KBr technique, in ATR spectrum



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show two bands (Fig. 1a). Band at  $3425\text{ cm}^{-1}$  was attributed to the symmetric  $\nu_1(\text{H}_2\text{O})$  and asymmetric  $\nu_3(\text{H}_2\text{O})$  stretching vibrations, while band at  $3223\text{ cm}^{-1}$  represent overtone of bending vibrations ( $2\nu_2(\text{H}_2\text{O})$ ) (He et al., 2007).

At the spectrum of the HDTMA bromide, in the region from  $3050\text{--}2800\text{ cm}^{-1}$ , several bands occur (Fig. 1b). Shoulder at  $3030\text{ cm}^{-1}$  and band at  $3018\text{ cm}^{-1}$  represent  $\nu_{\text{as}}(\text{N-CH}_3)$  vibrations (Madejova et al., 2009), although some authors state that this band at  $3018\text{ cm}^{-1}$  originate from  $\nu_{\text{s}}(\text{N-CH}_3)$  vibrations (Li et al., 2008). Shoulder at  $2945\text{ cm}^{-1}$  originates from overlapping  $\nu_{\text{s}}(\text{N-CH}_3)$  with  $\nu_{\text{as}}(\text{CH}_3)$  vibrations (Madejova et al., 2009). A small band at  $2870\text{ cm}^{-1}$  represent symmetric stretching vibrations  $\nu_{\text{s}}(\text{CH}_3)$  of methyl group which is not bonded to the N atom (Li et al., 2008; Madejova et al., 2009).

Most intensive absorption bands at  $2918\text{ cm}^{-1}$  and  $2850\text{ cm}^{-1}$  originate from asymmetric and symmetric stretching vibrations of  $\text{CH}_2$  group respectively (Tomić et al., 2015).

The interaction of NaM with HDTMA<sup>+</sup> cations caused the formation of new bands (Fig. 1c). Strong bands at  $2925\text{--}2927\text{ cm}^{-1}$  and  $2852\text{--}2854\text{ cm}^{-1}$  were assigned to asymmetric and symmetric stretching vibrations of  $\text{CH}_2$  group respectively (Tomić et al., 2015). Also, the band at  $3447\text{ cm}^{-1}$  in the spectrum of NaM, was shifted on lower wavenumbers ( $3433\text{ cm}^{-1}$ ) in the spectrum of HDTMA-montmorillonite, while the intensity of the band became significantly lower with the increment of HDTMA<sup>+</sup> loading (Fig. 1c). Interaction of HDTMA<sup>+</sup> with NaM caused the decrease of the water content due to the replacement of hydrated Na<sup>+</sup> with HDTMA<sup>+</sup>. Absorption bands around  $1473\text{ cm}^{-1}$  in the spectrum of the HDTMA bromide are attributed to  $\text{CH}_2$  scissoring vibrational mode (Fig. 1d). The nature of the montmorillonite surface was changed from hydrophilic to hydrophobic.

Stretching vibration bands of phenyl ring appear between  $1400$  and  $1600\text{ cm}^{-1}$  in the spectrum of PTMA, namely, at  $1594$ ,  $1500$ ,  $1474$ ,  $1461$ , and  $1416\text{ cm}^{-1}$  (Fig. 1f). The band at  $1300\text{ cm}^{-1}$  was assigned to the vibrations of the ammonium group. Heights of these bands decreased after the interaction between PTMA<sup>+</sup> cations and montmorillonite (Fig. 1e). The band at  $1594\text{ cm}^{-1}$  disappeared, probably as a result of the interaction between  $\pi$  electrons of the phenyl ring and  $\pi$  electrons of the oxygen in the tetrahedral layer of the montmorillonite (Majdan et al., 2009). Also, the band at  $1300\text{ cm}^{-1}$  disappeared, which is due to a strong interaction between positively charged nitrogen and negatively charged montmorillonite sites. These interactions result in a bond between the ammonium group and the montmorillonite surface.

### FTIR spectroscopy of samples with S-metolachlor

Three bands at  $1674$ ,  $1462$ , and  $1363\text{ cm}^{-1}$  in the spectrum of pure S-metolachlor were assigned to stretching vibrations of the carbonyl group ( $\text{C=O}$ ), phenyl group and anilidic group respectively (Fig. 2a) (El-Nahhal et al., 2001).

After the adsorption, the band assigned to  $\text{C=O}$  vibrations red-shifted from  $1674\text{ cm}^{-1}$  in the spectrum of S-metolachlor to  $1638\text{ cm}^{-1}$  in the NaM-SM spectrum, overlapping with the bending vibrations of water molecules in clay ( $1643\text{ cm}^{-1}$ ). The carbonyl double bond was weakened, almost despaired, after the sorption, indicating its involvement in the bonding process. Possible bonding interactions between montmorillonite and chloroacetanilide herbicide could include coordination bonds between  $\text{C=O}$  and the exchangeable cation, and/or H bonds between  $\text{C=O}$  and the hydration water because  $\text{C=O}$



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and C-N in this compound are in a conjugation mode due to the distribution of double bonds and lone electron pairs (Liu et al., 2002).

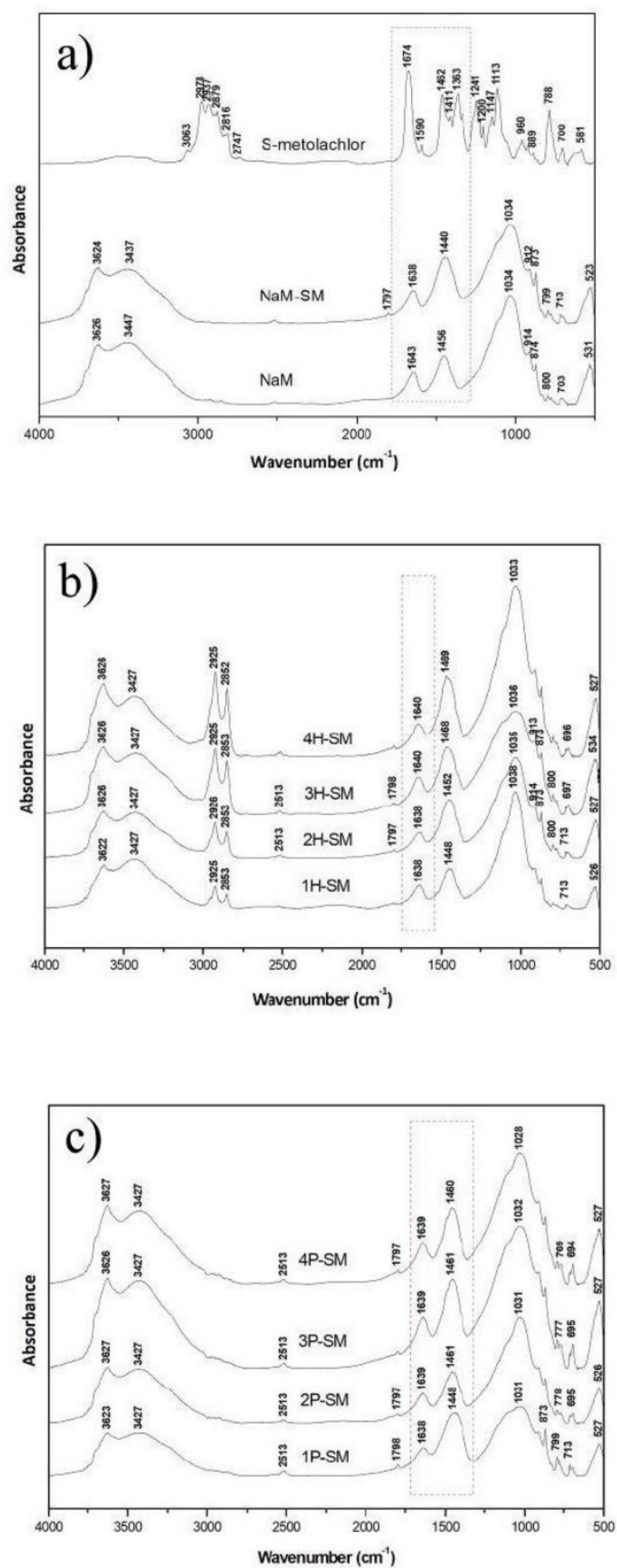


Figure 2. FTIR spectra of: a) S-metolachlor, Na-montmorillonite and Na-montmorillonite with adsorbed S-metolachlor; b) HDTMA-montmorillonite with adsorbed S-metolachlor; c) PTMA-montmorillonite with adsorbed S-metolachlor



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Both lone electron pairs on the oxygen of methoxy and ethoxy group are in resonance with the lone pair on nitrogen and the double C=O bond, which delocalizes the charge distribution and reduces the charge density on the carbonyl oxygen (Liu et al., 2000). The second significant change after the S-metolachlor sorption was detected on  $1456\text{ cm}^{-1}$  band. This band shifted to  $1440\text{ cm}^{-1}$  and increased in its intensity. This is the contribution of phenyl ring vibrations from the adsorbed herbicide.

Interaction of HDTMA-montmorillonite with S-metolachlor caused negligible changes in FTIR spectra. The absorption band of carbonyl group C=O in the spectrum of S-metolachlor ( $1674\text{ cm}^{-1}$ ) (Fig. 2a) shifted to lower wavenumbers ( $1638\text{--}1640\text{ cm}^{-1}$ ) (Fig. 2b). Band assigned to the ring vibrations in S-metolachlor ( $1462\text{ cm}^{-1}$ ) (Fig. 2a) was unclear for observation due to the HDTMA absorption bands that attributed to CH<sub>2</sub> scissoring vibrational mode and vibrations which were influenced by the presence of carbonates.

Interaction of PTMA-montmorillonite with S-metolachlor caused also negligible changes in FTIR spectra. The main differences between the spectrum of the pure S-metolachlor and S-metolachlor sorbed on PTMA-montmorillonite are: (1) shifting of the band at  $1674\text{ cm}^{-1}$  (C=O vibrations) to lower wavenumbers ( $1639\text{ cm}^{-1}$ ) after the sorption of the herbicide, (2) slightly movement of phenyl ring bands from  $1462\text{ cm}^{-1}$  to lower wavenumbers and (3) disappearance of  $1363\text{ cm}^{-1}$  band (C=C-N vibrations) after adsorption. According to the literature, one of the most important mechanisms of the herbicide adsorption on PTMA-montmorillonite is  $\pi$ - $\pi$  bonding between benzene the ring of the herbicide and aromatic ring of the PTMA<sup>+</sup> cation (Majdan et al., 2009).

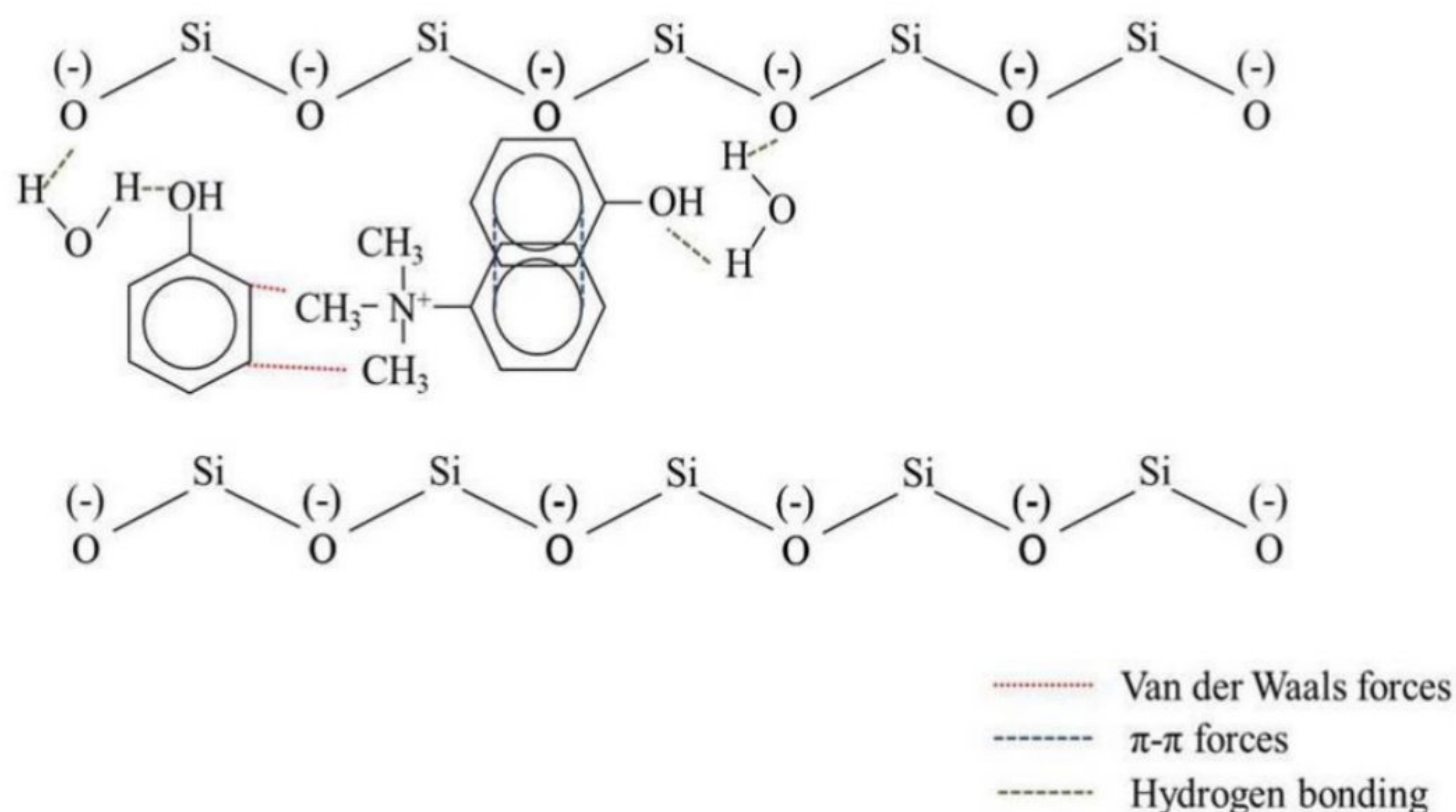


Figure 3. Suggested interactions between PTMA<sup>+</sup> cations and phenol in interlayer space of montmorillonite (Majdan et al., 2009)

## CONCLUSION

FTIR method was very useful in the process of examination of interactions between Na-montmorillonite and organic complexes such as HDTMA bromide and PTMA chloride.





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Adsorption of HDTMA<sup>+</sup> cations was easily detected by the occurrence of the stretching CH<sub>2</sub> vibrations. On the other hand, after the organic modification of the montmorillonite with the PTMA complex, stretching vibrations of phenyl ring occurred. The band associated with ammonium vibrations disappeared due to the interaction between the positive charge on nitrogen and the negative charge at the montmorillonite surface. Sorption of S-metolachlor on HDTMA-montmorillonites causes the redshift of the C=O absorption band which indicates that the C=O group participated in the formation of a bond with the HDTMA-montmorillonite. Adsorption of an aromatic compound such as S-metolachlor on PTMA-montmorillonite takes place, beside C=O group, through the interaction between the aromatic benzene ring of S-metolachlor and the aromatic benzene ring of the organic complex ( $\pi$ - $\pi$  bonds).

## ACKNOWLEDGMENT

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